

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-226722

(43)Date of publication of application : 21.08.2001

(51)Int.Cl.

C22C 1/00
// C22C 19/00
C22C 23/00
C22C 28/00
H01M 4/38

(21)Application number : 2000-035203

(71)Applicant : TOSHIBA CORP

(22)Date of filing : 14.02.2000

(72)Inventor : KAWASHIMA FUMIYUKI
ARAI TOMOHISA

(54) METHOD FOR PRODUCING HYDROGEN STORAGE ALLOY

(57)Abstract:

PROBLEM TO BE SOLVED: To suppress compositional variations caused by the evaporation of Mg at the time of producing a hydrogen storage alloy composed of Mg, Ni and rare earth elements as the main constituting elements, to facilitate the control of the alloy composition and moreover to increase the productivity on a level of mass-production.

SOLUTION: At the time of producing a hydrogen storage alloy composed of Mg, Ni and rare earth elements as the main constituting elements, a rare earth-Mg series master alloy is added to molten Ni or a molten rare earth-Ni series alloy to produce a rare earth-Mg-Ni series alloy having a desired composition. As the rare earth-Mg series master alloy, for example, an alloy containing Mg in a range of 1 to 95% by atomic ratio is used. As the molten metal for dissolving the rear earth-Mg series master alloy, for example, a molten rare earth-nickel series alloy containing rare earth elements in a range of 5 to 15% by atomic ratio is used.

*** NOTICES ***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention]This invention relates to the manufacturing method of the hydrogen storing metal alloy which uses magnesium, nickel, and a rare earth element as main composing elements.

[0002]

[Description of the Prior Art]The hydrogen storing metal alloy of a LaNi_5 system which is a rare earth-nickel system intermetallic compound which makes a CaCu_5 type crystal a main phase

as a nickel hydrogen secondary battery, Or the thing of a structure provided with the negative electrode containing the hydrogen storing metal alloy which makes a main phase Ti, Zr, and the Laves phase that contains V and nickel as a composing element is put in practical use.

[0003]Many rare earth-nickel system intermetallic compounds are considered as existence besides the LaNi_5 system. For example, it is indicated that the intermetallic compound which contains a rare earth element so much more than AB₅ type carries out occlusion of a lot of hydrogen near ordinary temperature than AB₅ type to Mat. Res. Bull., 11, and 1241 (1976). It is reported that the Mg-nickel-rare earth system alloy which has the presentation replaced by some rare earth elements of the rare earth-nickel system alloy with Mg carries out occlusion of a lot of hydrogen gas (for example, Yasuaki Osumi, soda and chlorine, 34, 447 (1983)).

[0004]Since an $\text{La}_{1-x}\text{Mg}_x\text{Ni}_2$ system alloy has high stability with hydrogen among the above-mentioned Mg-nickel-rare earth system alloys, there is a problem that the releasing speed of hydrogen is very small (J. Less-Common Met, 73, 339 (1980) references). Although the hydrogen storing metal alloy which has PuNi_3 structure by Mg_2LaNi_9 presentation is indicated to JP,11-217643,A, Although a hydrogen storage capacity also has many these Mg-

nickel-**** system alloys, it has the problem that the releasing speed of hydrogen is very small.

[0005]On the other hand, to JP,11-323469,A. Mg, nickel, and a rare earth element are used as main composing elements, compared with a LaNi_5 system hydrogen storing metal alloy, there is each of per volume and hydrogen storage capacities [many] per mass, and activation is quicker than a Laves phase system hydrogen storing metal alloy, and the hydrogen storing metal alloy excellent in the high charging and discharging characteristic is indicated. Compared with the rechargeable battery which it had, the negative electrode which contains a LaNi_5 system hydrogen storing metal alloy by using the negative pole material containing this hydrogen storing metal alloy with high capacity. And it becomes possible to manufacture the rechargeable battery which has a high charging and discharging characteristic superior to the rechargeable battery provided with the negative electrode containing a Laves phase system hydrogen storing metal alloy.

[0006]In manufacturing the hydrogen storing metal alloy which uses as main composing elements Mg, nickel, and a rare earth element which were described above, Since Mg metal cannot be directly added to an elevated-temperature molten metal, a rare earth-nickel system hardener and a Mg-nickel system hardener are used, for example as an alloy material, Weighing and after blending, it dissolves by high-frequency induction heating in an inert gas atmosphere, and casting to a metallic mold etc. is performed, so that it may become the composition ratio of a request of these.

[0007]

[Problem(s) to be Solved by the Invention]However, by the manufacturing method of the hydrogen storing metal alloy used as main composing elements, conventional Mg, nickel, and rare earth element. Since the Mg-nickel system hardener of the high-melting point is used as an alloy material, a melting temperature from it having to set up highly. In addition to being inferior to the productivity in a volume production level, there is a problem that the composition change of the alloy by evaporation of Mg is large, and control of alloy composition is difficult compared with a LaNi_5 system alloy.

[0008]In manufacturing the hydrogen storing metal alloy which was made in order to cope with such a technical problem, and uses Mg, nickel, and a rare earth element as main composing elements, this invention controls the composition change by evaporation of Mg, and makes control of alloy composition easy, and. It aims at providing the manufacturing method of the hydrogen storing metal alloy which made it possible to improve the productivity in a volume production level.

[0009]

[Means for Solving the Problem]As indicated to claim 1, a manufacturing method of a hydrogen

storing metal alloy of this invention Magnesium, In manufacturing a hydrogen storing metal alloy which uses nickel and a rare earth element as main composing elements, by adding a rare earth-magnesium system hardener to a nickel molten metal or a rare earth-nickel series molten metal, It is characterized by preparing a rare earth-magnesium nickel series alloy of a request presentation.

[0010]In a manufacturing method of a hydrogen storing metal alloy of this invention, as a hardener containing magnesium, Compared with the conventional magnesium nickel series hardener, a rare earth-magnesium system hardener of a low melting point is used, and a rare earth-magnesium nickel series alloy of a request presentation is prepared by adding this to a nickel molten metal or a rare earth-nickel series molten metal. Therefore, since molten metal temperature at the time of dissolving a hardener containing magnesium can be lowered, a composition change by evaporation of magnesium can be controlled and it becomes possible to be stabilized and to control alloy composition easily. Productivity in a volume production level can be improved.

[0011]As a manufacturing method of a hydrogen storing metal alloy of this invention was indicated to claim 2, it is an atomic ratio about magnesium. It is preferred to use a rare earth-magnesium system hardener contained in 1 - 95% of range. As for a rare earth-magnesium system hardener, as indicated to claim 3, it is preferred to have the melting point of the range of 600-1000 **. It becomes possible to obtain a rare earth-magnesium nickel series alloy of a request presentation often [accuracy] and easily by using a hardener which diluted magnesium with a rare earth element, and raised the melting point.

[0012]Although it is also possible to use nickel molten metal in a manufacturing method of a hydrogen storing metal alloy of this invention as a molten metal which dissolves a rare earth-magnesium system hardener, As indicated to claim 4, it is an atomic ratio about a rare earth element. By using a rare earth-nickel series molten metal included in 5 - 15% of range, it becomes possible to lower molten metal temperature further.

[0013]It is preferred to carry out a process of casting a molten metal of a rare earth-magnesium nickel series alloy of a request presentation in a manufacturing method of a hydrogen storing metal alloy of this invention as indicated to claim 5, and a process of heat-treating to an alloy after casting for uniformity and crystal structure control.

[0014]A manufacturing method of a hydrogen storing metal alloy of this invention is general formula:(Mg_{1-x}RE_x) (nickel_{1-y}T_y)_z (among a formula), as indicated to claim 6. RE is as being chosen out of a rare earth element containing Y as it is few. One sort of elements, T is as being chosen out of Co, Mn, Fe, aluminum, Ga, Zn, Sn, Cu, Si, Cr, and B as it is few. One sort of elements are shown, x, y, and z -- respectively -- a number with which it is satisfied of 0<x<1, 0<y<0.9, and 3.0<z<4.0 -- it is -- it is [as opposed to / especially / manufacture of a rare earth-magnesium nickel series alloy which has the presentation expressed substantially]

effective.

[0015]

[Embodiment of the Invention]Hereafter, the gestalt for carrying out this invention is explained.

[0016]In the manufacturing method of the hydrogen storing metal alloy of this invention, a rare earth-Mg system hardener is prepared first, this is supplied to nickel molten metal or a rare earth-nickel system molten metal, and the hydrogen storing metal alloy of a request presentation is prepared. Here, since the rare earth-Mg system hardener as a hardener containing Mg is a low melting point compared with the conventional Mg-nickel system hardener, it can lower the molten metal temperature at the time of dissolving the hardener containing Mg. Thereby, the composition change by evaporation of Mg can be controlled and it becomes possible to control desired alloy composition easily. The productivity in a volume production level can be improved.

[0017]The Mg content in the rare earth-Mg system hardener mentioned above is an atomic ratio. It is preferred to consider it as 1 to 95% of range. When there is too little Mg content in a rare earth-Mg system hardener, the amount of hardeners added into a molten metal increases, the fall of molten metal temperature is caused, and the dissolution and casting become difficult. On the other hand, when there is too much Mg content in a hardener, the melting point of a hardener approaches it of Mg and it becomes easy to produce bumping at the time of the addition to a molten metal. The Mg content in the rare earth-Mg system hardener from these things is an atomic ratio. It is preferred to set it as 1 to 95% of range, it is 10 to 80% of range more preferably, and is 20 to 70% of range still more preferably. As for the composition ratio of a rare earth element and Mg, it is preferred to choose the presentation near a eutectic crystal from the purpose for which the temperature of a molten metal is reduced.

[0018]When in manufacturing a rare earth-Mg system hardener controlling evaporation of Mg, and diluting Mg with a rare earth element and raising the melting point, it is the melting point of a rare earth-Mg system hardener. It is preferred to set it as the range of 600-1000 **. By setting it as the range which described the melting point of the hardener above, the rare earth-Mg system alloy of a request presentation can be obtained easily. The more desirable range of the rare earth-Mg system hardener melting point is 650-900 **.

[0019]As a rare earth element in a rare earth-Mg system hardener, It is that it is few as being chosen out of La, Ce, Pr, Nd, and Y which have hydrogen absorption ability. It is preferred to use one sort of elements, and it is more preferred the misch metal (Mm) which is a rare earth mixture further, and to use especially La Rich's misch metal (Lm).

[0020]It dissolves, for example by the high-frequency induction heating in the inside of an inert gas atmosphere, and it manufactures by casting to a metallic mold etc., and a rare earth-Mg system hardener which was mentioned above can also be manufactured from the mixed salt ghost of rare earth-magnesium, etc. using fused salt electrolysis. Specifically carry out

weighing and so that it may become a rare earth element and the composition ratio of a request of Mg for example, in an inert gas atmosphere like argon atmosphere, The rare earth-Mg system hardener of the purpose presentation is manufactured by making it dissolve by high-frequency induction heating using a magnesia crucible etc., and casting this to a metallic mold etc.

[0021]Next, using an above-mentioned rare earth-Mg system hardener, nickel, a rare earth element, etc., weighing is carried out so that it may become the rare earth-Mg-nickel system alloy composition of a request of these. Here, especially when the manufacturing method of this invention manufactures the rare earth-Mg-nickel system alloy which can apply Mg, nickel, and a rare earth element to the manufacture of various hydrogen storing metal alloys used as main composing elements or by which a presentation is especially expressed with the following general formula, it is effective.

[0022]

General formula: $(Mg_{1-x} RE_x) (nickel_{1-y} T_y)_z$ (among a formula) RE is as being chosen out of the rare earth element containing Y as it is few. One sort of elements, T is as being chosen out of Co, Mn, Fe, aluminum, Ga, Zn, Sn, Cu, Si, Cr, and B as it is few. One sort of elements are shown and x, y, and z are each. They are $0 < x < 1$, $0 < y < 0.9$, and a number with which it is satisfied of $3.0 < z < 4.0$.

The RE element in the above-mentioned general formula forms a crystal structure suitable for bearing hydrogen absorption ability and performing occlusion and discharge of nickel and its substituted element (T element), and hydrogen. From a viewpoint of attaining low cost-ization of a hydrogen storing metal alloy as a RE element, it is as being chosen out of La, Ce, Pr, Nd, and Y that it is few. It is preferred that they are one sort of elements. It is more preferred to use the misch metal which is a rare earth mixture as a RE element. as such a misch metal -- La -- a rich misch metal (Lm) is mentioned.

[0023]The amount x of substitution of the RE element to Mg 0 is exceeded. It is considered as less than one range. By making the amount x of substitution by a RE element into such a range, the hydrogen absorption and the burst size of a rare earth-Mg-nickel system alloy are raised, and initial activation can be raised. The amount x of substitution It is more desirable still more preferred to consider it as the range of 0.5-0.95. It is the range of 0.6-0.9.

[0024]T element is an ingredient which raises diffusion of the hydrogen which invaded in the alloy, and the catalysis in the surface. It is that it is few as being chosen out of T element which described above a part of nickel ingredient, i.e., Co, Mn, Fe, aluminum, Ga, Zn, Sn, Cu, Si, Cr, and B. By replacing by one sort of elements, the hydrogen absorption and the releasing speed of an alloy can be raised. Since T element is the element which does not react to hydrogen in generation of heat, i.e., the element which cannot make a hydride easily spontaneously, it is guessed that this is a thing resulting from the occlusion and discharge of a hydrogen storing

metal alloy becoming easy by addition of T element etc.

[0025]The amount y of substitution by T element such displacement effect It can obtain from the range exceeding 0. However, the amount y of substitution by T element of nickel ingredient When it becomes 0.9 or more, the crystal structure of a rare earth-Mg-nickel system alloy changes remarkably, and there is a possibility that the original characteristic of an alloy may be spoiled. Therefore, the amount y of substitution 0 is exceeded. It is considered as less than 0.9 range. It is more desirable still more preferred to consider it as the range of 0.005-0.8, and the ranges of the amount y of substitution are 0.01-0.6.

[0026]In the rare earth-Mg-nickel system alloy shown by the above-mentioned general formula, it is the total content z of nickel and T element (atomic ratio). 3.0 is exceeded. It is considered as less than 4.0 range. The range of the content z 3.0 is exceeded. By considering it as less than 4.0 range, it becomes possible to fully raise hydrogen absorption and emission characteristics, such as hydrogen absorption and a burst size of an alloy, and initial activation. Content z It is preferred to consider it as the range of 3.1-3.8.

[0027]Although it is also possible to use nickel molten metal as a molten metal which injects the rare earth-Mg system hardener mentioned above, in order to lower molten metal temperature, it is preferred to use a rare earth-nickel system molten metal. Specifically, it is an atomic ratio about rare earth content. By using the rare earth-nickel system molten metal made into 5 to 15% of range, It is abbreviation about molten metal temperature. It can be made to be able to fall by about 200 **, it can become possible to control more effectively evaporation of Mg after this adds a rare earth-Mg system hardener, and the composition control nature of a rare earth-Mg-nickel system alloy can be raised further.

[0028]In using a rare earth-nickel system molten metal, after dissolving only nickel by high-frequency induction heating in a vacuum first, the inside of a furnace is made into an inert gas atmosphere like argon atmosphere, and a rare earth element is added to this and it reduces molten metal temperature to it enough as a rare earth-nickel system molten metal. The presentation of the rare earth-nickel system molten metal at this time is an atomic ratio about rare earth content, as described above. It is preferred to set it as 5 - 15% of range. When T element replaces some nickel, it adds beforehand in this molten metal (a comb is nickel molten metal), and adds simultaneously with a rare earth-Mg system hardener.

[0029]In nickel molten metal which was mentioned above, or a rare earth-nickel system molten metal, the rare earth-Mg-nickel system molten metal of a request presentation is prepared by carrying out the specified quantity injection of the rare earth-Mg system hardener of prescribed composition. And such a rare earth-Mg-nickel system molten metal is cast, for example, and is alloyed. In order to control the segregation inside an alloy in alloying, it is preferred to use and cast a water-cooled rotating mold etc.

[0030]The rare earth-Mg-nickel system molten metal above-mentioned as the technique of

alloying It is also possible to apply the quenching method cooled and solidified at not less than 100 **/second in speed. A rare earth-Mg-nickel system alloy is specifically ejected from the molten state on the cooling body which carries out high speed movement, and the method of obtaining the thin band of about 10-300 micrometers of board thickness is mentioned. As such a quenching method, the single rolling method and the congruence rolling method are mentioned. By these methods, by setting up suitably conditions, such as construction material of molten metal temperature and a cooling roller, surface nature and the number of rotations of a cooling roller, cooling water temperature of a cooling roller, a nozzle diameter, and gas pressure, it is stabilized and an alloy can be manufactured. Techniques, such as a gas atomizing method, may be used in addition to the single rolling method or the congruence rolling method.

[0031]As for the rare earth-Mg-nickel system alloy obtained at an alloying process which was described above, it is preferred to heat-treat for acquiring the uniformity after casting and a desired crystal structure. An alloy main phase with a desired crystal structure here A $\text{Ce}_2\text{nickel}_7$ type, it is chosen out of the phase which has a CeNi_3 type, a Gd_2Co_7 type and one crystal structure of the PuNi_3 types, or a similar crystal structure -- at least -- It is the structure containing one phase.

[0032]As for heat treatment for uniformity and crystal structure control, it is preferred to be 300 or more ** and to carry out at the temperature of less than the melting point of an alloy in a vacuum or an inert atmosphere. When this heat treatment temperature is less than 300 **, while it becomes difficult to fully acquire the uniformity effect and the crystal structure control effect, when heat treatment temperature becomes more than the melting point of an alloy, the composition change by oxidation and Mg evaporation of a rare earth element etc., etc. will be caused.

[0033]the above-mentioned heat treatment process specifically injects a rare earth-Mg-nickel system alloy into a vacuum heat treatment furnace first -- after carrying out evacuation to a 1×10^{-4} Pa grade -- for example -- Temperature up is carried out to 300 **, and argon gas is introduced in a furnace. As for the ambient pressure by argon gas, in order to control evaporation of Mg, being referred to as about 0.1 MPa is preferred. Then, temperature up of the inside of a furnace is carried out to treatment temperature, and it heat-treats by carrying out predetermined time maintenance.

[0034]heat treatment temperature -- concrete -- it is preferred to set it as the range of 600-1100 ** -- further -- It is preferred to consider it as the range of 800-1000 **. When heat treating time is less than 10 minutes, and crystallization becomes uneven and exceeds 10 hours on the other hand, oxidation of an alloy surface, It is [that it is preferred to consider it as the range from 10 minutes to 10 hours as for heat treating time since there is a possibility that the

composition change by Mg evaporation may become large, and] more desirable. It is the range of 5 to 10 hours. It is preferred to use evaporation of Mg under heat treatment for a ***** sake for the tight box made from graphite, etc.

[0035]In the manufacturing method of the hydrogen storing metal alloy of this invention which was mentioned above, as a hardener containing Mg, since the rare earth-Mg system hardener of the low melting point is used, the molten metal temperature at the time of dissolving this hardener can be lowered. Under the present circumstances, molten metal temperature can be further lowered by using a rare earth-nickel system molten metal as a molten metal which injects a rare earth-Mg system hardener.

[0036]By these, since it becomes possible to control the composition change by evaporation of Mg, the rare earth-Mg-nickel system hydrogen storing metal alloy which has desired alloy composition can be easily obtained by being stabilized. This contributes to improvement and stabilization of the characteristic of a hydrogen storing metal alloy greatly. Since the fall of molten metal temperature leads to improvement in the productivity in a volume production level, it becomes possible to reduce the manufacturing cost of a rare earth-Mg-nickel system hydrogen storing metal alloy.

[0037]

[Example]Next, the concrete example of this invention and its evaluation result are described.

[0038]Examples 1-10 and the comparative examples 1-2 -- weighing of a rare earth element and Mg was carried out, respectively, and these were supplied to the magnesia crucible so that it might become the presentation of the rare earth-Mg system hardener shown in the following table 1 first. After fully carrying out evacuation of the inside of a fusion furnace, the rare earth-Mg system hardener ingot was obtained, respectively by introducing argon gas to 0.1MPa in a furnace, and dissolving these each raw material in high-frequency induction heating. the misch metal (Lm) in Table 1 -- La of 93 atom % , Ce of one atom % , and Pr of three atom % -- and -- It consists of Nd of three atom % .

[0039]Next, weighing of the raw material of the rare earth-Mg system hardener, rare earth element and misch metal which were obtained, respectively, and others was carried out so that it might become the presentation of the rare earth-Mg-nickel system alloy shown in the following table 1. Only each raw material of nickel, Fe, and Co was thrown in in the magnesia crucible, and other raw materials were set to the cup for addition, respectively.

[0040]After carrying out evacuation of the inside of a fusion furnace, only nickel in a crucible, Fe, and Co were first dissolved by high-frequency induction heating in the vacuum.

Subsequently, argon gas was introduced to 0.1MPa in the furnace, the rare earth element and misch metal which were set to the cup for addition into this molten metal were added, and the rare earth-nickel system molten metal was obtained, respectively.

[0041]After fully reducing the temperature of each rare earth-nickel system molten metal, a

rare earth-Mg system hardener and other elements were added. After fully agitating such a rare earth-Mg-nickel system molten metal, the rare earth-Mg-nickel system alloy ingot was obtained by casting to a water cooling mold, respectively.

[0042]The quantitative analysis of each obtained alloy ingot was carried out with internal standard ICP emission spectrometry and nickel dimethylglyoxime weight method, Mg of these each alloy and the content of the rare earth element were quantified, and the decrement was written together to Table 1. The decrement of Mg and a rare earth element was calculated here by /(amount of Mg at time of combination) x100(%) (the rare earth element content of the quantified alloy) / (the amount of rare earth elements at the time of combination) x100 (%), respectively (Mg content in the quantified alloy).

[0043]A Mg-nickel system hardener is used for the comparative examples 1 and 2 in Table 1 as a hardener containing Mg.

[0044]

[Table 1]

	Mg-希土類系母合金組成	希土類-Mg-Ni系合金組成	Mgの減少量(%)	希土類元素の減少量(%)
実施例 1	Mg0.45La0.55	(Mg0.30La0.70)(Ni0.95Co0.03Al0.02)3.6	2.1	1.1
実施例 2	Mg0.30La0.70	(Mg0.20La0.80)(Ni0.94Co0.02Al0.02Mn0.02)3.7	1.8	1.0
実施例 3	Mg0.40La0.45Y0.15	(Mg0.20La0.70Y0.10)(Ni0.96Co0.03Al0.01)3.4	1.7	0.9
実施例 4	Mg0.30Lm0.70	(Mg0.10Lm0.90)(Ni0.94Co0.03Cu0.02B0.01)3.5	1.5	0.8
実施例 5	Mg0.70Lm0.30	(Mg0.60Lm0.40)(Ni0.95Co0.04Fe0.01)3.8	2.3	1.2
実施例 6	Mg0.50Lm0.50	(Mg0.25Lm0.75)(Ni0.94Co0.03Al0.02Zn0.01)3.3	1.7	0.9
実施例 7	Mg0.45Lm0.40Y0.15	(Mg0.25Lm0.65Y0.10)(Ni0.96Co0.02Al0.01Ga0.01)3.8	1.8	1.0
実施例 8	Mg0.55Lm0.45	(Mg0.35Lm0.65)(Ni0.94Al0.03Mn0.02Sn0.01)3.5	2.0	1.1
実施例 9	Mg0.60Lm0.40	(Mg0.45Lm0.55)(Ni0.97Co0.02Si0.01)3.4	2.1	1.1
実施例 10	Mg0.40Lm0.60	(Mg0.20Mn0.80)(Ni0.94Co0.03Al0.02B0.01)3.9	1.7	0.8
比較例 1	Mg0.33Ni0.67	(Mg0.30Lm0.70)(Ni0.95Co0.02Al0.03)3.5	13.5	7.5
比較例 2	Mg0.67Ni0.33	(Mg0.25Lm0.75)(Ni0.04Fe0.94Al0.02)3.4	21.3	8.1

[0045]. Alloyed by adding a rare earth-Mg system hardener to nickel molten metal or a rare earth-nickel system molten metal so that clearly from Table 1. The rare earth-Mg-nickel system hydrogen storing metal alloy of Examples 1-10 has few amounts of evaporation of Mg compared with the alloy of the comparative examples 1-2, and it turns out that the composition change is controlled. It is because the Mg-nickel system hardener is used for the thing with large Mg amount of evaporation of the alloy of the comparative examples 1 and 2.

[0046]Examples 11-23 and the comparative examples 3-4 -- so that it may become the presentation of the rare earth-Mg system hardener shown in the following table 2 first, The rare earth-Mg system hardener ingot was obtained, respectively by carrying out weighing of a rare earth element and Mg, respectively, and dissolving these each raw material with the high frequency induction furnace which introduced argon gas to 0.1MPa. The misch metal (Lm) in Table 2 consists of La of 55 atom % , Ce of one atom %, Pr of 11 atom % , and Nd of 33 atom

% .

[0047]Next, weighing of the raw material of the rare earth-Mg system hardener, rare earth element and misch metal which were obtained, respectively, and others was carried out so that it might become the presentation of the rare earth-Mg-nickel system alloy shown in the following table 2. Only each raw material of nickel, Fe, and Co was thrown in in the magnesia crucible, and other raw materials were set to the cup for addition, respectively.

[0048]After carrying out evacuation of the inside of a fusion furnace, only nickel in a crucible, Fe, and Co were first dissolved by high-frequency induction heating in the vacuum.

Subsequently, argon gas was introduced to 0.1MPa in the furnace, the rare earth element and misch metal which were set to the cup for addition into this molten metal were added, and the rare earth-nickel system molten metal was obtained, respectively.

[0049]After fully reducing the temperature of each rare earth-nickel system molten metal, a rare earth-Mg system hardener and other elements were added. After fully agitating such a rare earth-Mg-nickel system molten metal, the rare earth-Mg-nickel system alloy ingot was obtained by casting to a water cooling mold, respectively.

[0050]These each alloy ingot is set all over the tight box made from graphite, and it is in argon atmosphere. It heat-treated on the conditions of 980 °C x 10 hours. Thus, the quantitative analysis of each obtained alloy ingot was carried out by chelatometry and the ICP method, Mg of these each alloy and the content of the rare earth element were quantified, and those decrements were written together to Table 2. The decrement of Mg and a rare earth element was calculated like Example 1.

[0051]Then, coarse grinding of each above-mentioned alloy ingot was carried out, and it classified in the particle size of 75 micrometers or less at the screen through the pulverized powder obtained by pulverizing with a hammermill further. About each hydrogen storing metal alloy powder, the crystal structure of the main phase was identified by powder X-ray diffractometry. The crystal structure of each example was written together to Table 2.

[0052]A Mg-nickel system hardener and Mg-rare earth system hardener are used for the comparative examples 3 and 4 in Table 2 as a hardener containing Mg.

[0053]Next, in order to evaluate the characteristic as a battery material of the hydrogen storing metal alloy by above-mentioned Examples 11-23 and the comparative examples 3 and 4, the electrode using each cell service-water matter occlusion alloy was formed in the procedure as shown below, and the service capacity and the charge-and-discharge cycle life of these each electrode were measured.

[0054]First, it is a weight ratio about each alloy powder and the end of electrolytic copper powder. It mixes at a rate of 1:1, a tablet making machine (10 mm in inside diameter) is used for 1 g of this mixture, and it is by the pressure of about 10^3 MPa. The pellet was produced by pressurizing for 5 minutes, respectively. Put these each pellet with nickel net producing object,

and spot welding of the circumference was carried out, and the alloy electrode (negative electrode) was produced by carrying out spot welding of the lead of nickel, respectively.

[0055] Subsequently, each obtained negative electrode was immersed in an 8-N potassium hydroxide solution with the sintering type nickel electrode which is a counter electrode, respectively, and the cell of negative-electrode capacity regulation was constituted, respectively. They are these per [hydrogen storing metal alloy 1g] in a 25 ** thermostat. Per [after charging for 3 hours and stopping for 10 minutes with 200-mA current (200mA/(g)) / hydrogen storing metal alloy 1g] A mercury oxide electrode is received with 100-mA current. The charge-and-discharge cycle test which discharges until it is set to -0.5V was done.

[0056] The measurement result of the maximum service capacity in a charge-and-discharge cycle test and a charge-and-discharge cycle life (service capacity is the maximum service capacity the number of cycles at the time of falling to 80%) was written together to Table 2.

[0057]

[Table 2]

	Mg—希土類系母合金組成	希土類-Mg-Ni系合金組成	Mgの減少量(%)	希土類元素の減少量(%)	主相の結晶構造	放電容量(mAh/g)	サイクル寿命(サイクル)
実施例 11	Mg0.50La0.50	(Mg0.25La0.75)(Ni0.94Co0.04Mn0.02)3.4	2.1	1.0	Ce2Ni7	384	530
実施例 12	Mg0.35La0.60Y0.05	(Mg0.24La0.75Y0.01)(Ni0.97Co0.02Al0.01)3.6	1.8	0.8	CeNi3	412	580
実施例 13	Mg0.30La0.60Nd0.10	(Mg0.20La0.75Nd0.05)(Ni0.96Co0.02Al0.01Si0.01)3.4	1.7	0.8	Ce2Ni7	430	545
実施例 14	Mg0.25La0.75	(Mg0.10La0.90)(Ni0.94Co0.04Cu0.01B0.01)3.5	1.5	0.7	Ce2Ni7	393	518
実施例 15	Mg0.80La0.20	(Mg0.60La0.40)(Ni0.95Co0.04Fe0.01)3.4	2.3	1.1	PuNi3	388	563
実施例 16	Mg0.50La0.50	(Mg0.25La0.75)(Ni0.94Co0.03Al0.02Zn0.01)3.6	1.7	0.9	Ce2Ni7	425	540
実施例 17	Mg0.40La0.60	(Mg0.25La0.75)(Ni0.96Co0.03Ga0.01)3.8	1.8	1.0	CeNi3	404	532
実施例 18	Mg0.70La0.30	(Mg0.35La0.65)(Ni0.94Co0.03Al0.02Sn0.01)3.7	2.0	1.2	Ce2Ni7	390	528
実施例 19	Mg0.50La0.50	(Mg0.45La0.55)(Ni0.96Co0.02Si0.01Cr0.01)3.4	2.1	1.1	PuNi3	387	543
実施例 20	Mg0.35La0.65	(Mg0.25La0.75)(Ni0.94Co0.03Al0.02B0.01)3.5	1.7	1.0	CeNi3	423	538
実施例 21	Mg0.65La0.35	(Mg0.55La0.45)(Ni0.98Co0.01Al0.01)3.6	1.8	1.0	PuNi3	402	553
実施例 22	Mg0.30La0.60Y0.10	(Mg0.25La0.70Y0.05)(Ni0.92Co0.04Al0.02Fe0.02)3.4	1.6	0.9	Gd2Co7	397	573
実施例 23	Mg0.30La0.70	(Mg0.25La0.75)(Ni0.94Co0.03Al0.02Cr0.01)3.5	1.3	0.8	Ce2Ni7	413	534
比較例 3	Mg0.33Ni0.67	(Mg0.25La0.75)(Ni0.96Al0.02Mn0.02)3.4	12.8	6.8	Ce2Ni7	320	412
比較例 4	Mg0.40La0.60	(Mg0.20La0.80)(Ni0.98Co0.01Al0.01)1.8	1.6	0.9	MgCu2	120	372

[0058]. Alloyed by adding a rare earth-Mg system hardener to nickel molten metal or a rare earth-nickel system molten metal so that clearly from Table 2. The rare earth-Mg-nickel system hydrogen storing metal alloy of Examples 11-23 has few amounts of evaporation of Mg compared with the alloy of the comparative example 3, and it turns out that a composition change is controlled and high service capacity is obtained.

[0059] In the alloy of the comparative example 3, it is because the thing with large Mg amount of evaporation uses the Mg-nickel system hardener, without using a rare earth-Mg system hardener. The total content of nickel and T element the thing with small service capacity of the rare earth-Mg-nickel system hydrogen storing metal alloy of the comparative example 4 It is because it is three or less.

[0060]

[Effect of the Invention]As explained above, according to the manufacturing method of the hydrogen storing metal alloy of this invention, since the composition change by evaporation of Mg can be controlled, it becomes possible to be stabilized and to control easily, the presentation of the hydrogen storing metal alloy which uses Mg, nickel, and a rare earth element as main composing elements. This contributes to improvement and stabilization of the characteristic of a hydrogen storing metal alloy greatly. Since the molten metal temperature at the time of hydrogen storing metal alloy production can be lowered, it becomes possible to reduce the productivity in a volume production level, and by extension, a manufacturing cost.

[Translation done.]

*** NOTICES ***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1]In manufacturing a hydrogen storing metal alloy which uses magnesium, nickel, and a rare earth element as main composing elements, by adding a rare earth-magnesium system hardener to a nickel molten metal or a rare earth-nickel series molten metal, A manufacturing method of a hydrogen storing metal alloy preparing a rare earth-magnesium nickel series alloy of a request presentation.

[Claim 2]In a manufacturing method of the hydrogen storing metal alloy according to claim 1, said rare earth-magnesium system hardener is an atomic ratio about magnesium. A manufacturing method of a hydrogen storing metal alloy containing in 1 - 95% of range.

[Claim 3]A manufacturing method of a hydrogen storing metal alloy having the melting point of said rare earth-magnesium system hardener and the range of 600-1000 ** in a manufacturing method of the hydrogen storing metal alloy according to claim 1.

[Claim 4]It is an atomic ratio about a rare earth element as a molten metal which adds said rare earth-magnesium system hardener in a manufacturing method of the hydrogen storing metal alloy according to claim 1. A manufacturing method of a hydrogen storing metal alloy using said rare earth-nickel series molten metal included in 5 - 15% of range.

[Claim 5]A manufacturing method of the hydrogen storing metal alloy according to claim 1 characterized by comprising the following.

A process of casting a molten metal of a rare earth-magnesium nickel series alloy of said request presentation.

A process of heat-treating to an alloy after said casting for uniformity and crystal structure control.

[Claim 6]In a manufacturing method of the hydrogen storing metal alloy according to claim 1, said rare earth-magnesium nickel series alloy, A general formula: $(Mg_{1-x}RE_x)(nickel_{1-y}T_y)_z$

(among a formula) RE is as being chosen out of a rare earth element containing Y as it is few. One sort of elements, T is as being chosen out of Co, Mn, Fe, aluminum, Ga, Zn, Sn, Cu, Si, Cr, and B as it is few. One sort of elements are shown, a number with which x, y, and z are satisfied of $0 < x < 1$, $0 < y < 0.9$, and $3.0 < z < 4.0$, respectively -- it is -- a manufacturing method of a hydrogen storing metal alloy having the presentation expressed substantially.

[Translation done.]